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Representation of polygalacturonic acid by subunits in the analysis of its potentiometric titration curves

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Abstract

The potentiometric titration curves of aqueous solutions of polygalacturonic acid were determined in the presence of either tetraalkylammonium or alkaline ions in order to explain the effects of the size and the nature of the counterion on the degree of dissociation. In the evaluation of potentiometric curves, the approach proposed by Strauss was used and successive ionization constants of appropriately chosen oligomeric subunits of the polymer molecule were determined. The partition functions and Gibbs free energies of ionization per mole of polygalacturonic acid at the ambient chemical potential of hydrogen ions, and the Gibbs free energies per mole of polyacid related to the hydrogen ion in its standard state, were calculated and are given as a function of hydrogen ion activity or of the degree of ionization. From the above functions the differences in the counterion specificities were observed and are discussed on the basis of the formation of contact ion pairs between an alkaline ion and the carboxylate group. In addition, the values of the entropy and enthalpy changes per mole of repeating unit (hydrogen ion at standard state potential) accompanying the stepwise dissociation reactions were calculated on the basis of the temperature dependence of the stepwise dissociation constants via the Gibbs–Helmholtz relation, and the thermodynamic data were correlated with the structural properties of the investigated polymer solute.

Keywords: Counterion; Deprotonation; PGA; Polygalacturonic acid; Subunit; Thermodynamics; Titration

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1. Introduction

The physical, biochemical, and functional properties of pectin are of great interest to a diverse cross-section of scientists and technologists because pectin can be classified as a polyelectrolyte, a complex polysaccharide, an important food fibre, a major plant cell wall component, and a ubiquitous nutritional factor and gelling agent in foods [1]. In spite of numerous investigations in this field, the structure of pectin has not yet been definitively explained. Therefore, several recent research works have been concerned with the investigation of aqueous solutions of poly(α-D)-galacturonic acid, i.e. pectic acid, which can be isolated by enzymatic or alkaline-catalysed hydrolysis from pectin. Some authors have already concerned themselves with the acid–base properties of similar systems in order to investigate the effect of partial neutralization on the structural properties of polyacids in aqueous solutions, and the effect brought about by the addition or exchange of counterions [2,3]. For polygalacturonic acid (PGA), there are few data of this kind in the literature, especially in connection with a possible conformational transition.

In the present study, the potentiometric titration curves of aqueous solutions of PGA were determined in the presence of tetramethylammonium ($(CH_3)_4N^+$) or tetrabutylammonium ($(C_4H_9)_4N^+$), lithium (Li^+), sodium (Na^+) and potassium (K^+) ions, with the aim of elucidating the effects of the size of the alkyl groups and the nature of the counterion on the degree and extent of dissociation. In the evaluation of potentiometric curves, the method of Strauss [4,5] was used to obtain more insight into the possible conformational transition; this method has not yet previously been applied to pectic acid.

2. Experimental

Commercially available PGA was purchased from Fluka Chemie. The degree of esterification of the methyl ester of PGA (5.34%) was determined acidimetrically after hydrolysing the ester with sodium hydroxide [6]. The viscosity-average molecular weight (30115) was estimated on the basis of the Mark–Houwnik relation using the necessary constants from Ref. [7]. Considering the molecular weight of the monomeric unit, D-galacturonic acid (206.53), the average degree of polymerization was determined to be 146. The total equivalent polymer concentration was measured by potentiometric hydrogen ion titration using Gran's procedure [8] for the evaluation of the potentiometric curves. From the equivalent weight thus determined, the mole fraction of polygalacturonate was calculated and found to be 0.85. To obtain an aqueous solution of PGA, insoluble pectic acid was converted to its soluble sodium salt and then percolated through a cation-exchange resin (DOWEX 50 WX 8) in the H^+ form [9].

All potentiometric titrations were performed in three parallel determinations at 298.15 ± 0.05 K, and also with lithium hydroxide at 308.15 and 313.15 K. Equal additions of 0.10 mol dm^{-3} LiOH, NaOH, KOH, $(CH_3)_4NOH$ and $(C_4H_9)_4NOH$ were carried out by means of a burette (accuracy ± 0.025 cm^3) and protection against carbon dioxide was secured. The pH or electrical potential of the investigated solutions was recorded using a pH-meter (Radiometer, type pH M4d) with a glass combined electrode (Radiometer, type GK 2501 C). The pH-meter was standardized with six standard buffers (range pH 3–10) [10].

3. Results and discussion

Because a detailed account of the method has been given by Strauss et al. [4,5], only a brief summary of the essential steps will be presented here.

The ionization of a polyacid molecule or a polyacid subunit, containing N acidic groups may be described by the equations

$$AH_N \rightleftharpoons A^{-i}_{N-i} + iH^+ \qquad 1 \le i \le N \tag{1}$$

and the overall dissociation constants may be defined by

$$\beta_i = \frac{[AH^{-i}_{N-i}]}{[AH_N]h^i} \qquad 0 \le i \le N \tag{2}$$

where $[AH_N]$ denotes the concentrations of un-ionized and $[AH^{-i}_{N-i}]$ the ionized polyacid molecular species, and the quantity h is the antilogarithm of the pH and represents the reciprocal of the hyrodgen ion activity ($\mathrm{pH} = \log h$; $h = a^{-1}_{\mathrm{H}^+}$). Note that $\beta_0 = 1$. The degree of deprotonation α is provided by the potentiometric titration curve and is defined by the equation

$$\alpha = \frac{\alpha_m}{N} \frac{\sum_{i=1}^{N} i\beta_i h^i}{1 + \sum_{i=1}^{N} \beta_i h^i} = \frac{[\mathrm{BOH}] + [\mathrm{H}^+] - [\mathrm{OH}^-]}{c_a} \tag{3}$$

where α_m denotes the degree of deprotonation at complete deprotonation, i.e. the number of acidic groups per repeat unit of polyacid or subunit, [BOH] is the number of moles of base added per dm^3 solution, $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ the molarities of free hydrogen and hydroxyl ions, and c_a the concentration of polyacid in monomoles per dm^3, i.e. the amount (in mol) of ionizable groups per dm^3. Now the mole fraction of the polyacid or subunit species with i dissociated protons x_i can be defined as

$$x_i = \frac{[AH^{-i}_{N-i}]}{\sum_{j=0}^{N} [AH^{-j}_{N-j}]} \qquad 0 \le i \le N \tag{4}$$

or on combination of Eqs. (2) and (4) by

$$x_i = \frac{\beta_i h^i}{\sum_{j=0}^{N} \beta_j h^j} \qquad 0 \le i \le N \tag{5}$$

The average number of dissociated protons per polyacid or polyacid subunit species is given by

$$\langle i \rangle = \sum_{j=1}^{N} (j - \langle i \rangle) \beta_j h^j \tag{6}$$

The value of $\langle i \rangle$ is dependent on α via the relation

$$\langle i \rangle = N \frac{\alpha}{\alpha_m} \tag{7}$$

Therefore, from N experimental (α,pH) data pairs, we can obtain N pairs of ($\langle i \rangle$,h) values, which when substituted into Eq. (6) produce N linear equations from which N parameters β_i ($1 \leq i \leq N$) may be determined. When the overall ionization constants β_i are known, a species population distribution can be derived at any stage of the titration and the stepwise ionization constants K_i can be calculated

$$K_i = \frac{\beta_i}{\beta_{i-1}} \tag{8}$$

The minimum number of parameters needed to describe the titration curve of PGA was found to be $N = 6$. From $N = 6$ experimental pairs (α,pH), we obtain six linear equations from which the six parameters β_i were determined by the Gauss–Jordan elimination method (HP model 10, MATH PAC IV − 1). The relevance of the adopted model was tested by calculating, by means of the known values of β_i, the value of α corresponding to each experimental pH value and comparing this calculated value of α with the experimental one. The differences were less than 0.002; a perfect fit of the theoretical curve to the experimental points can also be seen in Fig. 1. The overall, as well as stepwise, ionization constants for PGA with subunit size $N = 6$, determined in the presence of different counterions, are presented in Table 1. On the basis of the experimental results shown in Table 1, one can conclude that for the investigated system, the values of pβ_1 depend on the nature of the counterion, which can be explained by the formation of contact ion

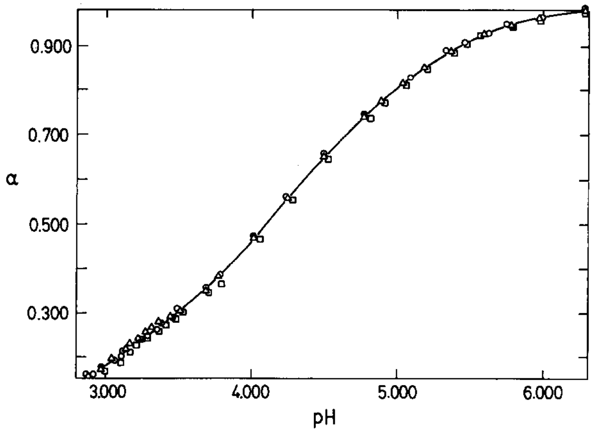

Fig. 1. Change in the degree of deprotonation α with pH. Titration of PGA with 0.100 mol dm^{-3} LiOH at 298.15 K; $c_a = 10.66$ mmol dm^{-3}.

Table 1
Value of the overall and stepwise dissociation constants for PGA at 298.15 K for different counterions

Counterion	i	β_i	$\mathrm{p}\beta_i$	$\mathrm{p}K_i$
Li^+	1	1.636×10^{-3}	2.786	2.786
	2	1.075×10^{-6}	5.969	3.182
	3	8.177×10^{-11}	10.087	4.119
	4	6.057×10^{-15}	14.218	4.130
	5	9.978×10^{-20}	19.001	4.783
	6	4.935×10^{-25}	24.307	5.306
Na^+	1	2.351×10^{-3}	2.629	2.629
	2	1.242×10^{-6}	5.906	3.277
	3	1.255×10^{-10}	9.901	3.995
	4	8.690×10^{-15}	14.061	4.160
	5	1.989×10^{-19}	18.701	4.640
	6	9.011×10^{-25}	24.045	5.344
K^+	1	3.386×10^{-3}	2.470	2.470
	2	1.800×10^{-6}	5.745	3.274
	3	1.821×10^{-10}	9.740	3.995
	4	1.181×10^{-14}	13.928	4.188
	5	2.766×10^{-19}	18.558	4.630
	6	1.148×10^{-24}	23.940	5.382
$(CH_3)_4N^+$	1	5.457×10^{-3}	2.263	2.263
	2	1.231×10^{-6}	5.910	3.647
	3	1.967×10^{-10}	9.706	3.796
	4	5.719×10^{-15}	14.243	4.536
	5	8.038×10^{-20}	19.095	4.852
	6	1.699×10^{-25}	24.770	5.675
$(C_4H_9)_4N^+$	1	5.118×10^{-3}	2.291	2.291
	2	1.558×10^{-6}	5.807	3.517
	3	1.853×10^{-10}	9.732	3.925
	4	4.652×10^{-15}	14.332	4.600
	5	3.010×10^{-20}	19.521	5.189
	6	2.073×10^{-26}	25.683	6.162

pairs between an alkaline ion and the carboxylate group. The observed binding order $K^+ < Na^+ < Li^+$ has also been inferred from potentiometric titrations of other polycarboxylic polymers, e.g. polyacrylic [11] and polymethacrylic acid [12]. If the binding process is solely a consequence of Coulombic interactions of the counterions with the electrical field of a polyion, then for a series of univalent counterions one would expect decreased binding with increasing hydrated counterion radius. In this case site binding is thought to be accompanied by partial desolvation of the hydrated cations as the carboxylate group replaces one or more water ligands of the alkaline counterion. The desolvated alkali metal ions would be expected to bind in the sequence observed, i.e. inversely with the known sequence of their crystallographic radii. The bond between the carboxylate group and the lithium ion is more covalent than in the case of potassium, in accordance with the

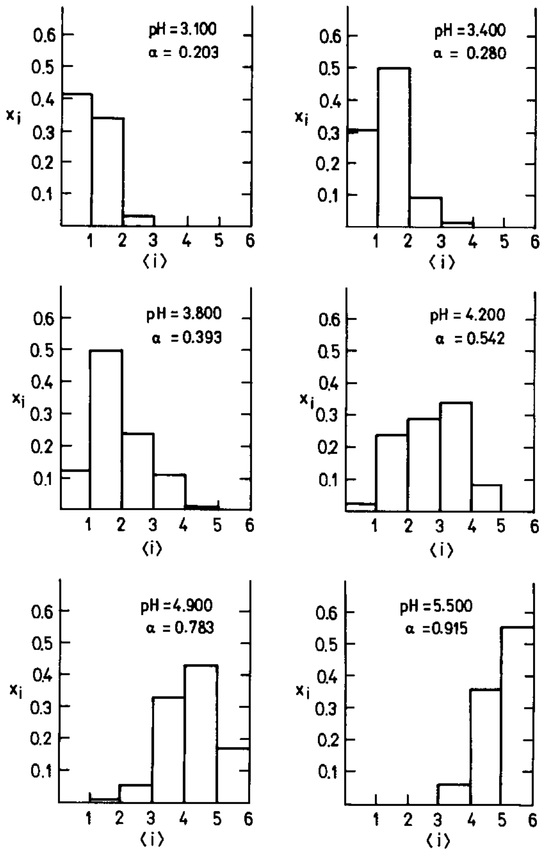

Fig. 2. Plots of the species population functions (species mole fractions x_i vs. average number of dissociated protons $\langle i \rangle$) at different degrees of deprotonation α at 298.15 K; counterion, Li^+.

higher ionic potential of the lithium ion. This supposition has been confirmed by infrared absorption spectroscopy for the alkaline salts of pectic acid, recently performed in our laboratory [13].

The values of the overall and stepwise dissociation constants ($p\beta_i$, pK_i) for PGA partly neutralized with tetraalkylammonium bases show a slight dependence on the radius of the counterion. The values of the successive deprotonation constants increase with increasing radius of the hydrophobic counterion for each value of i between 3 and 6. At low degrees of deprotonation when species with a small number of dissociated protons predominate in solution (Fig. 2), the size of the $(CH_3)_4N^+$ ion in comparison with the $(C_4H_9)_4N^+$ ion and delocalization of the positive charge on the $(CH_3)_4N^+$ ion is probably the deciding factor for stronger interaction with the polyion. With increasing charge on the chain, the effect of shading by the counterions should be of great importance for the dissociation of each additional proton. For an ion such as $(C_4H_9)_4N^+$, this is offset to some extent by the four longer alkyl groups that protect the positive charge of the rigid sphere [14].

Table 2
Species mole fractions for PGA at 298.15 K; counterion Li^+

α	pH	i						
		0	1	2	3	4	5	6
0.20	3.10	0.20	0.42	0.35	0.03			
0.28	3.40	0.07	0.31	0.51	0.10	0.02		
0.39	3.80	0.01	0.12	0.50	0.24	0.11	0.01	
0.54	4.20		0.02	0.24	0.29	0.34	0.09	0.01
0.78	4.90			0.01	0.06	0.33	0.43	0.17
0.92	5.50					0.07	0.36	0.57

For PGA, the pK_i values increase steadily with increasing i, indicating according to Strauss [5] the absence of a conformational transition during the titration. The data in Table 2 for the species mole fractions x_i at different stages of titration and the species population distribution (Fig. 2) support the conclusion mentioned above.

As shown in Fig. 2, with increasing degree of deprotonation α, the single maximum of the species distribution shifts gradually to higher values of i. The unimodal distribution for PGA (a single peak only, irrespective of the counterion) allows comparison with the results for polyacrylic acid, and is in contrast to those for polymethacrylic and polyethacrylic acid, which both show the bimodal distribution of types of polymers known to display a pH-induced conformational transition [15].

The Gibbs free energy of deprotonation per mole of polyacid (the hydrogen ion at its ambient chemical potential in the equilibrium mixture) is defined as [5]

$$\Delta G_p^* = -RT \ln \Sigma^* \tag{9}$$

An asterisk is used to denote symbols pertaining to the whole polyacid molecule. The partition function of the polyacid molecule is defined as

$$\Sigma^* = 1 + \sum_{i=1}^{N^*} \beta_i^* h^i = \left(1 + \sum_{i=1}^{N} \beta_i h^i\right)^{N^*/N} \tag{10}$$

The partition function of the polyacid molecule Σ^* is represented as a power of Σ_N. This assumes that the polyacid molecule consists of independent non-interacting subunits containing N carboxylic groups. Σ_N is the partition function of the subunit, i.e. any chain segment containing N ionizable groups. The Gibbs free energy per mole of polyacid (the hydrogen ion in its standard state) is [5]

$$\Delta G_p^{\ominus *} = -RT\left(\ln \Sigma^* - \frac{N^*\alpha}{\alpha_m} \ln h\right) \tag{11}$$

The Gibbs free energies per mole of repeating unit, ΔG and $\Delta G^{\ominus}$, referring to

Table 3
Values of the Gibbs free energy per mole of repeating unit (hydrogen ion at ambient state chemical potential or at standard state chemical potential) for PGA as a function of log *h* and degree of deprotonation at 298.15 K for different counterions

Counterion	log *h*	α	$-\Delta G$ in kJ mol^{-1}	$\Delta G^{\ominus}$ in kJ mol^{-1}
Li^+	3.100	0.203	0.660	2.932
	3.600	0.333	1.423	5.419
	4.200	0.542	2.898	10.095
	4.800	0.754	5.138	15.519
	5.200	0.858	6.984	18.481
	5.600	0.930	9.032	20.694
Na^+	3.100	0.208	0.754	2.926
	3.600	0.340	1.528	5.459
	4.200	0.562	3.051	10.421
	4.800	0.772	5.359	15.791
	5.200	0.866	7.234	18.469
	5.600	0.930	9.288	20.438
K^+	3.100	0.219	0.885	2.990
	3.600	0.341	1.676	5.331
	4.200	0.558	3.193	10.184
	4.800	0.769	5.489	15.579
	5.200	0.862	7.356	18.228
	5.600	0.926	9.402	20.196
$(CH_3)_4N^+$	3.100	0.196	0.961	2.507
	3.600	0.309	1.664	4.685
	4.200	0.505	3.054	9.052
	4.800	0.696	5.112	13.956
	5.200	0.805	6.831	17.062
	5.600	0.885	8.765	19.522
$(C_4H_9)_4N^+$	3.100	0.203	0.963	2.629
	3.600	0.310	1.684	4.686
	4.200	0.478	3.031	8.428
	4.800	0.638	4.946	12.533
	5.200	0.734	6.515	15.270
	5.600	0.814	8.285	17.733

hydrogen ion at ambient and standard state potential, are [5]

$$\frac{\Delta G}{RT} = -\left(\frac{\alpha_m}{N}\right) \ln \Sigma_N \qquad (12)$$

$$\frac{\Delta G^{\ominus}}{RT} = -\left(\frac{\alpha_m}{N}\right) \ln \Sigma_N + \alpha \ln h \qquad (13)$$

Changes in the Gibbs free energy per mole of repeating unit for PGA with log *h* at 298.15 K for different counterions are given in Table 3 and are shown in Fig. 3. From Table 3, it is clear that the absolute value of the Gibbs free energy per mole of repeating unit (hydrogen ion at ambient state chemical potential) increases with increasing ionic radius of the alkaline ion, while the Gibbs free energy per mole of

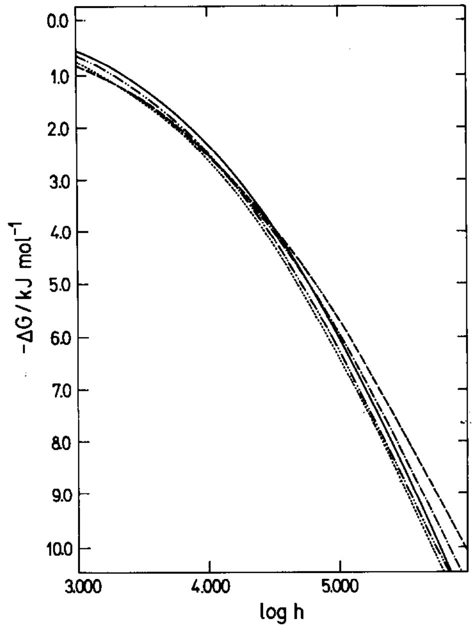

Fig. 3. Change in the Gibbs free energy of deprotonation of PGA per mole of repeating unit (hydrogen ion at ambient state chemical potential) with log *h* at 298.15 K: counterion Li^+ (—); Na^+ (– · · –); K^+ (· · ·); $(CH_3)_4N^+$ (– · –); and $(C_4H_9)_4N^+$ (– –).

Table 4
Values of overall and stepwise dissociation constants for PGA in the temperature range studied; counterion, Li^+

T in K	*i*	β_i	$p\beta_i$	pK_i
298.15	1	1.636×10^{-3}	2.786	2.786
	2	1.075×10^{-6}	5.969	3.182
	3	8.177×10^{-11}	10.087	4.119
	4	6.057×10^{-15}	14.218	4.130
	5	9.978×10^{-20}	19.001	4.783
	6	4.935×10^{-25}	24.307	5.306
308.15	1	1.662×10^{-3}	2.779	2.779
	2	9.502×10^{-7}	6.022	3.243
	3	1.054×10^{-10}	9.977	3.955
	4	4.860×10^{-15}	14.313	4.336
	5	7.367×10^{-20}	19.133	4.819
	6	2.877×10^{-25}	24.541	5.408
313.15	1	1.556×10^{-3}	2.808	2.808
	2	8.722×10^{-7}	6.059	3.251
	3	9.798×10^{-11}	10.009	3.949
	4	3.402×10^{-15}	14.468	4.459
	5	6.769×10^{-20}	19.169	4.701
	6	2.315×10^{-25}	24.635	5.466

repeating unit (hydrogen ion at standard state chemical potential) is independent of the ionic radius of the alkaline ion.

The temperature dependence of the deprotonation constants (β_i, K_i) calculated by the adopted model is given in Table 4. From the data in Table 4, it may be concluded that the constants are only slightly temperature-dependent; the values for $p\beta_1$ are equal within experimental error and the average value $\overline{p\beta_1}$ equals 2.791 ± 0.015.

Taking into account the experimental data from Table 4, $\Delta G^\ominus$ values for the system investigated were calculated from relation (13) at a definite temperature for several degrees of deprotonation. The data for $\Delta G^\ominus$ for PGA as a function of temperature can be fitted with straight lines at each degree of deprotonation. Their slope, $\partial \Delta G^\ominus / \partial T$ is, of course, equal to $-\Delta S^\ominus$, i.e. the entropy of deprotonation of polyacid per mole of repeating unit (hydrogen ion at standard state chemical potential). Finally, the values of the enthalpy of deprotonation of polyacid per mole of repeating unit (hydrogen ion at standard state chemical potential) can be calculated via the Gibbs–Helmholtz relation

$$\Delta H^\ominus = \Delta G^\ominus + T\Delta S^\ominus \tag{14}$$

The error in the Gibbs free energy $\delta\Delta G^\ominus$ was estimated via the relation [16]

$$(\delta\Delta G^\ominus)^2 = (2.303RT\mathrm{pH})^2(\delta\alpha)^2 + (2.303\alpha RT)^2(\delta\mathrm{pH})^2 + \left[-\frac{R}{6}\left(\ln\Sigma_N + T\frac{\partial \ln\Sigma_N}{\partial T}\right) + 2.303\alpha R\mathrm{pH}\right]^2(\delta T)^2 \tag{15}$$

where $\delta\alpha$, δpH, δT are the errors of parameters in Eq. (13). The error in the enthalpy changes for the deprotonation process per mole of repeating unit was

Table 5
Values of the Gibbs free energy of deprotonation of PGA per mole of repeating unit (hydrogen ion at standard state chemical potential) as a function of degree of deprotonation in the temperature range studied; counterion, Li$^+$

α	T in K	$\Delta G^\ominus$ in kJ mol^{-1}
0.250	298.15	3.788 ± 0.056
	308.15	3.928 ± 0.058
	313.15	4.022 ± 0.059
0.500	298.15	9.101 ± 0.070
	308.15	9.416 ± 0.073
	313.15	9.630 ± 0.075
0.700	298.15	14.072 ± 0.079
	308.15	14.619 ± 0.083
	313.15	14.941 ± 0.085
0.850	298.15	18.246 ± 0.089
	308.15	19.007 ± 0.093
	313.15	19.391 ± 0.094
0.950	298.15	21.343 ± 0.099
	308.15	22.260 ± 0.104
	313.15	22.702 ± 0.106

Table 6
Values of enthalpy and entropy of deprotonation of PGA per mole of repeating unit (hydrogen ion at standard state potential) as a function of the degree of deprotonation at 298.15 K; counterion, Li^+

α	$-\Delta H^\ominus$ in kJ mol^{-1}	$-\Delta S^\ominus$ in kJ mol^{-1} K^{-1}
0.250	0.795 ± 0.074	0.0154 ± 0.0012
0.500	1.258 ± 0.108	0.0347 ± 0.0027
0.700	3.068 ± 0.141	0.0575 ± 0.0023
0.850	4.492 ± 0.028	0.0763 ± 0.0001
0.950	5.725 ± 0.078	0.0908 ± 0.0008

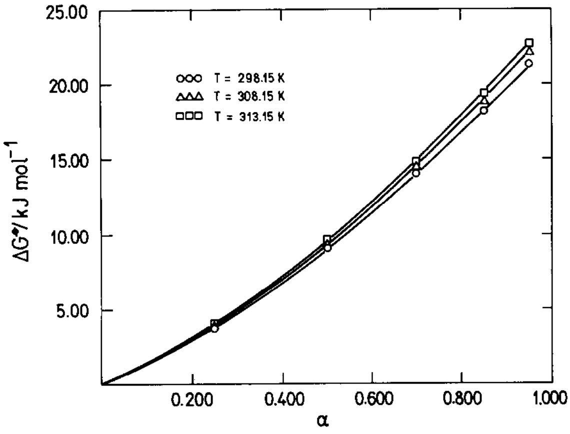

Fig. 4. Change in the Gibbs free energy of deprotonation of PGA per mole of repeating unit (hydrogen ion at standard state chemical potential) with the degree of deprotonation in the temperature range studied; counterion, Li^+.

obtained as follows:

$$\frac{\delta\Delta H^\ominus}{\Delta H^\ominus}=\frac{\delta\Delta G^\ominus}{\Delta G^\ominus}+\frac{\delta T}{T}+\frac{\delta\Delta S^\ominus}{\Delta S^\ominus} \tag{16}$$

The calculated values of $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ are given in Tables 5 and 6. In Fig. 4, the dependence of the Gibbs free energy function on the degrees of deprotonation is shown as a function of temperature.

The values of $\Delta G^\ominus$ are positive, while the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ become more and more negative with increasing degree of deprotonation. Both the enthalpy and entropy of dissociation of polymeric weak acids are known to be sensitive functions mainly of the charge density, and the trend of $\Delta H^\ominus$ and $\Delta S^\ominus$ of PGA is entirely due to the polyelectrolytic nature of the chain.

From the small differences in the values of $\Delta G^\ominus$ at a definite α for different temperatures, it follows that some compensation of the enthalpic and entropic values of the thermodynamic functions in the process of deprotonation of PGA

Table 7
Degree of deprotonation and temperature dependence of the partition function of the subunit Σ_N for PGA

α	T in K	$\ln \Sigma_N$	$\partial \ln \Sigma_N / \partial T$
0.250	298.15	2.16	0.000
	308.15	2.16	
	313.15	2.13	
0.500	298.15	6.26	0.016
	308.15	6.42	
	313.15	6.50	
0.700	298.15	10.67	0.030
	308.15	11.27	
	313.15	11.05	
0.850	298.15	16.48	0.025
	308.15	17.05	
	313.15	16.78	
0.950	298.15	23.76	0.093
	308.15	24.83	
	313.15	25.12	

occurs. Because of the small temperature dependence of the deprotonation constants for the appropriate oligomer subunit or its partition function $\partial \ln \Sigma_N / \partial T$ (see Table 7), relation (13) was not applied for derivation of the respective thermodynamic functions, i.e. the enthalpy and entropy of deprotonation.

The above arguments suggest that aqueous solutions of the discussed polyacid are rather complicated systems. The literature differences referring to a conformational transition of this macromolecular solute [17–19] should be ascribed to the differences in its conformational properties. Incorporation of L-rhamnopyranosyl units into the galacturonan chain leads to a change in orientation of the molecules joined in the chain, and severely kinks the chain [20]; one group of authors reported that L-rhamnopyranosyl units are quite unevenly distributed within the galacturonan backbone [21]. In addition, the effect of the degree of esterification on the chain comformation is not negligible. Therefore, the phenomenon of conformational transition in different samples of PGA, i.e. pectic acid, could be more or less evident. However, Cesaro et al. [19] indicate that the very small energy change on transition ΔG_{tr} is probably the reason for the lack of evidence of an intramolecular conformational transition from the pH data.

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